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<p>Pine oil type concentrate compositions and cleaning compositions providing sanitizing effects comprise a germicidal active cationic surfactant, a co-solvent, a non-ionic surfactant system, and generally include a relatively high amount of fragrance and/or fragrance adjuvant compositions. The preferred embodiments of the pine oil type cleaning compositions provide the benefits of good cleaning, effective sanitizing action, good blooming upon addition to an excess of water and long lasting fragrance, and low irritancy levels notwithstanding the relatively high levels of organic solvents comprised in the compositions.</p>		<table border="1"> <caption>Bar Chart Data</caption> <thead> <tr> <th>Category</th> <th>C1 (%)</th> <th>E1 (%)</th> </tr> </thead> <tbody> <tr> <td>1</td> <td>~45</td> <td>~55</td> </tr> <tr> <td>2</td> <td>~15</td> <td>~85</td> </tr> <tr> <td>3</td> <td>~35</td> <td>~65</td> </tr> </tbody> </table>		Category	C1 (%)	E1 (%)	1	~45	~55	2	~15	~85	3	~35	~65
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IMPROVED COMPOSITIONS CONTAINING ORGANIC COMPOUNDS

The present invention relates to improvements in cleaning compositions. More particularly, the present invention is directed to improved pine oil type cleaning compositions and concentrates thereof, which find particular use in hard surface cleaning applications.

One particular category of cleaning compositions are those which are classed as pine oil type cleaning compositions, such typically contain one or more resins or oils derived from coniferous species of trees, and typically generate a milky or cloudy appearance when diluted with water in dilutions useful for cleaning applications. Such pine oil type cleaning compositions are generally provided in a concentrated composition which is subsequently diluted with water by an end user/consumer to form a cleaning composition therefrom. However, pine oils also are known to leave undesirable surface residues, particularly on hard surfaces and are further known irritants particularly to the eyes, skin and mucous tissues. Also, pine oil, while known to have cleaning efficacy is not generally considered useful as a broad spectrum antibacterial or sanitizing agent.

It is among the objects of the present invention to provide improved pine oil type cleaning compositions in a "concentrate" form which exhibit one or more of the identifying characteristics outlined above, especially a pronounced blooming effect, and an effective sanitizing effect and a long lasting scent while having reduced amounts of pine oil in such compositions. According to a further aspect of the invention there are provided "cleaning compositions", i.e., aqueous dilutions of these improved pine oil type cleaning compositions which exhibit good blooming upon being produced, and which provide an effective cleaning and/or sanitizing benefit to hard surfaces.

These and other objects of the invention will become apparent from the following detailed description of the invention.

The compositions according to the invention comprise the following constituents:

- A) a pine oil preparation containing at least about 60% alpha-terpineol;
- B) a co-solvent;
- C) a non-ionic surfactant system which desirably includes two or more non-ionic surfactants wherein at least one of which exhibits a cloud point of 20°C or less in water;
- D) at least one cationic quaternary ammonium surfactant which exhibits germicidal activity;
- E) fragrance/fragrance enhancer; and,
- F) water.

In addition to the above described constituents, the compositions according to the invention may optionally further include known art additives in conventional amounts.

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The inventors have found that it is now possible to produce certain concentrate compositions utilizing these selected constituents in particular formulations which provide pine oil type cleaning compositions in a concentrated liquid form which unlike many known prior art composition further include a germicidal effect, good blooming and a high concentration of fragrance and/or fragrance solubilizer constituents. Surprisingly however, these inventive compositions still exhibit many of the desirable characteristics of pine oil type cleaning compositions described above, especially "blooming", notwithstanding the relatively high levels of fragrance and/or fragrance solubilizer constituents which they comprise. This is an important and surprising feature of the invention as the use of relatively higher amounts of fragrance and/or fragrance solubilizer constituents, which are known to be organic constituents, would be expected to significantly diminish or deactivate the desirable "blooming" effect when such concentrates are further diluted with water. The "blooming" observed may be described as the change of the water's appearance from essentially colorless and transparent to that of a milky white or milky yellowish white, cloudy appearance. That such behaviour is achieved in the compositions according to the present invention, which contain relatively high amounts of fragrance and/or fragrance solubilizer constituents, is surprising to say the least.

Constituent A) Compositions according to the invention comprise a pine oil constituent. Pine oil is an organic solvent, and is a complex blend of oils, alcohols, acids, esters, aldehydes and other organic compounds. These include terpenes which include a large number of related alcohols or ketones. Some important constituents include terpineol, which is one of three isomeric alcohols having the basic molecular formula $C_{10}H_{17}OH$. Useful pine oils include synthetic pine oil, and also include steam distilled and sulfate pine oils, and will generally contain a higher content of turpentine alcohols. Other important compounds include alpha- and beta-pinene (turpentine), abietic acid (rosin), and other isoprene derivatives.

Particularly effective pine oils which are presently commercially available include Glidco® Pine Oil™ 60 (believed to contain approximately 60% terpene alcohols), Glidco® Pine Oil 80 (believed to contain approximately 80% terpene alcohols) Glidco® Pine Oil 150 (believed to contain approximately 85% terpene alcohols); Glidco® Terpene SW (believed to contain approximately 75% terpene alcohols); as well as Glidco® Terpineol 350 (believed to contain approximately 100% terpene alcohols). Each of these may be obtained from available from Glidco Organics Corp., Jacksonville, FL (USA). Other products which can contain up to 100% pure alpha-terpineol, may also be used in the present invention.

The pine oil constituent may be present in the concentrate compositions in amounts of from about 0.001 % by weight to up to about 15% by weight, preferably about 4 - 12 % by weight, most

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preferably in amount of between 6 - 10 % pine oil by weight. Preferred of these are pine oil preparations which comprise at least about 60% terpene alcohols, and more preferably those which comprise at least about 80% terpene alcohols. As with all of the weight percentages of the constituents described, the weight percentages are indicative of the weight percentages of the actives in a constituent containing preparation.

Constituent B) A further constituent according to the invention is a co-solvent which is present in addition to the pine oil which is itself known to be an organic solvent and assists in improves the dispersability and/or miscibility of the water insoluble pine oil in water. The co-solvent may also improve the miscibility of further constituents according to the present invention, including any water insoluble or poorly soluble constituents. Many useful co-solvents which are known to be useful in dispersing pine oil in water may be used as Constituent B, especially those based on are based on organic solvents; virutally any may be used as long as it does not undesirably disrupt the favorable characteristics of the invention, especially the blooming characteristic. Mixtures of two or more co-solvents may also be used as Constituent B.

Exemplary co-solvents useful as Constituent B include certain glycols and glycol ethers which exhibit the above described properties. Examples of such glycol ethers include those having the general structure $R_9-O-R_{10}-OH$, wherein R_9 is an alkoxy of 1 to 20 carbon atoms, or aryloxy of at least 6 carbon atoms, and R_{10} is an ether condensate of propylene glycol and/or ethylene glycol having from one to ten glycol monomer units. Examples of such useful glycol ethers include propylene glycol methyl ether, dipropylene glycol methyl ether, tripropylene glycol methyl ether, propylene glycol isobutyl ether, ethylene glycol methyl ether, ethylene glycol ethyl ether, ethylene glycol butyl ether, diethylene glycol phenyl ether, propylene glycol phenol ether, and mixtures thereof. Preferred are ethylene glycol n-butyl ether, diethylene glycol n-butyl ether, and mixtures thereof. Such glycol ethers are presently commercially available from a number of sources including in the DOWANOL™ glycol ether from The Dow Chemical Company, Midland MI (USA).

Further exemplary co-solvents useful as Constituent B include C_1-C_8 alcohols, especially C_1-C_3 alcohols, of which isopropanol is preferred.

It has generally been found the addition of only a minimum effective amount which is found to be effective in dispersing or solubilizing the pine oil constituent and any other aqueous insoluble or poorly soluble constituents in the concentrate compositions is desirably used. Such is due to desire to reduce the amount of volatile organic constituents in the concentrate compositions of the invention, which volatile organic constituents are desirably minimized from an environmental standpoint. The present inventors have found that inclusion of the solubilizing agent according to Constituent B in amounts of about 0.001% by weight to about 15 % by weight have been found to be

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effective to solubilize the pine oil, as well as in solubilizing other less water soluble constituents present in the concentrate compositions of the invention. Preferably, the solubilizing agent of Constituent B is present in amounts 4 - 12% by weight, and most preferably 8 - 10% by weight.

Constituent C) The concentrate compositions according to the invention include a nonionic surfactant system which comprises a mixture of two or more nonionic surfactants which includes a first nonionic surfactant constituent which is a single or is a mixture of nonionic surfactants which exhibit a cloud point of 20°C or less in water, and a second nonionic surfactant constituent which includes a single nonionic surfactant or mixture of surfactants which are useful in solubilizing the first nonionic surfactant constituent in water. The first said nonionic surfactant constituent is generally selected to be one or more aqueous insoluble or poorly soluble nonionic, which optionally, but further very desirably exhibit a cloud point of 20°C or less in water. The second nonionic to solubilize the first nonionic surfactant. Such a solubilizing effect aids in the long term shelf stability of prepared concentrated compositions, and in ensuring the optical clarity of concentrated compositions especially during the shelf life of prepared concentrated compositions.

Generally, suitable nonionic surface active agents which may be used in the nonionic surfactant system according to Constituent C includes condensation products of one or more alkylene oxide groups with an organic hydrophobic compound, such as an aliphatic or alkyl aromatic compound. Exemplary suitable nonionic surface active agents include surfactant compositions based upon polyethoxylated, polypropoxylated, or polyglycerolated alcohols, alkylphenols or fatty acids.

One exemplary class of nonionic surfactants useful in Constituent C according to the instant invention include certain alkoxylated linear aliphatic alcohol surfactants which are believed to be the condensation products of a C₈-C₁₀ hydrophilic moiety with polyethylene oxide/polypropylene oxide moieties. Such alkoxylated linear alcohol surfactants are presently commercially available under the tradename Poly-Tergent® (Olin Chemical Co., Stamford CT) and of these particularly useful are those which are marketed as Poly-Tergent® SL-22, Poly-Tergent® SL-42, Poly-Tergent® SL-62 and Poly-Tergent® SL-29, of which Poly-Tergent® SL-62 is particularly advantageous. Poly-Tergent® SL-42 is described as being a moderately foaming, biodegradable alkoxylated linear alcohol surfactant having on average 5 moles of oxyethylene groups per molecule. Poly-Tergent® SL-62 is described as being a moderately foaming, biodegradable alkoxylated linear alcohol surfactant having on average 8 moles of oxyethylene groups per molecule. These alkoxylated linear alcohol surfactants provide good deterative action in the removal of many types of fats and greases such as are frequently found in soils on hard surfaces, as well as providing a further solubilizing effects..

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A further exemplary class of nonionic surfactants which finds use are alkoxyated alcohols especially alkoxyated fatty alcohols. These include ethoxyated and propoxyated fatty alcohols, as well as ethoxyated and propoxyated alkyl phenols, having both with alkyl chains of about 7-16, more preferably about 8-13 carbon chains in length. Exemplary alkoxyated alcohols include certain

5 ethoxyated alcohol compositions presently commercially available from the Shell Chemical Company, (Houston, TX) under the general trade name Neodol®, which are described to be linear alcohol ethoxylates. Of these, those exhibiting a cloud point of 20°C or less may be used. Specific compositions include: Neodol® 91-2.5 which is described as an ethoxyated alcohol having an average molar ratio of 2.7:1 ethoxy groups/alcohol groups per molecule; a molecular weight of 281,

10 and a cloud point in water of 20°C and less; Neodol® 23-3 which is described as an ethoxyated alcohol having an average molar ratio of 2.9:1 ethoxy groups/alcohol groups per molecule; a molecular weight of 322, and a cloud point in water of 20°C and less.

Exemplary alkoxyated alcohols further include compositions commercially available from the Union Carbide Co., (Danbury, CT) under the general trade name Tergitol®, which are described

15 to be secondary alcohol ethoxylates. Again, those exhibiting a cloud point of 20°C and less may be used. Specific compositions include: Tergitol® 15-S-3 described as an ethoxyated secondary alcohol having an average molar ratio of 3.2:1 ethoxy groups/alcohol groups per molecule, and a cloud point in water of less than 20°C; Tergitol® 15-S-5 described as an ethoxyated secondary alcohol having an average molar ratio of 5:1 ethoxy groups/alcohol groups per molecule, and a cloud

20 point in water of less than 20°C.

Further exemplary nonionic surfactants which may be used in Constituent C include certain alkanolamides including monoethanolamides and diethanolamides, particularly fatty monoalkanolamides and fatty dialkanolamides. Commercially available monoethanol amides and diethanol amides include those marketed under the trade names Alakamide® and Cyclomide® by

25 Rhône-Poulenc Co., (Cranbury, NJ). These include surfactants based on coconut diethanolamides; coconut monoethanolamides; 2:1 modified coconut monoethanolamide; fatty acid diethanolamides; lauric/linoleic diethanolamides; linoleic diethanolamides; lauric monoethanolamides; lauric diethanolamides; lauric/myristic diethanolamides; oleic diethanolamide; stearic diethanolamides; coconut diethanolamides; lauric monoisopropanolamides; stearic monoethanolamides;

30 diethanolamides of unsaturated fatty acids; alkanolamides which may be used singly, or in mixtures. Particularly useful are lineolic diethanolamides and lauric diethanolamides.

Exemplary alkoxyated alkyl phenols useful in Constituent C include certain compositions presently commercially available from the Rhône-Poulenc Co., (Cranbury, NJ) under the general trade name Igepal®, which are described to be octyl and nonyl phenols. Again, those exhibiting a

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cloud point of 20°C or less may be used. These include Igepal® CA-210 an ethoxylated octyl phenol having an average of 1.5 ethoxy groups groups per molecule and a cloud point in water of less than 20°C and, Igepal® CA-420 an ethoxylated octyl phenol having an average of 3 ethoxy groups groups per molecule and a cloud point in water of less than 20°C.

5 Especially preferred for use as the first nonionic surfactant constituent which comprises Constituent C according to the instant invention is Neodol® 91-2.5 which is described as an ethoxylated alcohol having an average molar ratio of 2.7:1 ethoxy groups/alcohol groups per molecule; a molecular weight of 281, and a cloud point in water of 20°C and less.

10 Of course, a mixture of two or more nonionic surfactants having a cloud point of 20°C or less may be incorporated into the inventive compositions. Other known nonionic surface active agents not particularly enumerated here may also be used.

The cloud point of the first nonionic surfactant constituent according to Constituent C of the present invention may be determined by known methods, such as by ASTM D2024 (reapproved 1986) for "Standard Test method for Cloud Point of Nonionic Surfactants". An even simpler test method for effectively determining which nonionic surfactants may be used as the first nonionic surfactant constituent in the compositions of the invention is as follows: to a clean beaker or other glass vessel is added 99 parts by weight of deionized water at 20°C ± 0.5°C, and 1 part by weight (by weight of the actives) of a surfactant composition to be tested. This test sample is stirred and the temperature permitted to drop to 20°C; if this test sample is observed to be murky or cloudy in appearance as the test sample's temperature achieves 20°C and drops below 20°C, it is considered to have a suitable cloud point of 20°C and less and may be used as Constituent B in the concentrate compositions according to the invention.

25 Constituent C, may be present in any effective amount, but desirably is present in the concentrate compositions from about 0.001 % by weight to about 25% by weight, preferably 0.1 - 20% by weight, and most preferably from 8% and 15% by weight. Desirably, particularly where Constituent C includes an alkanolamide, dialkanolamide or trialkanolamide, Constituent C) is present in a weight percentage about equal to, or greater than the amount of Constituent E) present in the concentrate composition.

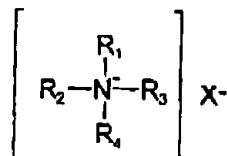
30 Constituent D) The concentrate compositions according to the invention include as a necessary constituent at least one cationic quaternary ammonium surfactant which is found to provide a broad antibacterial or sanitizing function. Such materials are per se, known to the art.

Exemplary useful and preferred compounds are quaternary ammonium compounds and salts thereof, which may be characterized by the general structural formula:

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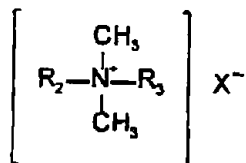
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where at least one of R_1 , R_2 , R_3 and R_4 is a hydrophobic, aliphatic, aryl aliphatic or aliphatic aryl radical of from 6 to 26 carbon atoms, and the entire cation portion of the molecule has a molecular weight of at least 165. The hydrophobic radicals may be long-chain alkyl, long-chain alkoxy aryl, long-chain alkyl aryl, halogen-substituted long-chain alkyl aryl, long-chain alkyl phenoxy alkyl, aryl alkyl, etc. The remaining radicals on the nitrogen atoms other than the hydrophobic radicals are substituents of a hydrocarbon structure usually containing a total of no more than 12 carbon atoms. The radicals R_1 , R_2 , R_3 and R_4 may be straight chained or may be branched, but are preferably straight chained, and may include one or more amide or ether linkages. The radical X may be any salt-forming anionic radical.

Exemplary quarternary ammonium salts within the above description include the alkyl ammonium halides such as cetyl trimethyl ammonium bromide, alkyl aryl ammonium halides such as octadecyl dimethyl benzyl ammonium bromide, N-alkyl pyridinium halides such as N-cetyl pyridinium bromide, and the like. Other suitable types of quarternary ammonium salts include those in which the molecule contains either amide or ether linkages such as octyl phenoxy ethoxy ethyl dimethyl benzyl ammonium chloride, N-(laurylcocoaminoformylmethyl)-pyridinium chloride, and the like. Other very effective types of quarternary ammonium compounds which are useful as germicides include those in which the hydrophobic radical is characterized by a substituted aromatic nucleus as in the case of lauryloxyphenyltrimethyl ammonium chloride, cetylaminophenyltrimethyl ammonium methosulfate, dodecylphenyltrimethyl ammonium methosulfate, dodecylbenzyltrimethyl ammonium chloride, chlorinated dodecylbenzyltrimethyl ammonium chloride, and the like.

Especially Preferred quarternary ammonium compounds which act as germicides and which are be found useful in the practice of the present invention include those which have the structural formula:



wherein R_2 and R_3 are the same or different C_8 - C_{12} alkyl, or R_2 is C_{12} - C_{16} alkyl, C_8 - C_{12} alkylethoxy, C_8 - C_{12} alkylphenoylethoxy and R_3 is benzyl, and X is a halide, for example chloride, bromide or

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iodide, or methosulfate. The alkyl groups recited in R_2 and R_3 may be straight chained or branched, but are preferably substantially linear.

Such quaternary germicides are commercially available either as single quaternary ammonium compounds or as mixtures of two or more different quaternaries. Suitable materials include germicidal quaternary ammonium compounds include those sold under the tradenames BARDAC, BARQUAT and HYAMINE (Lonza Inc., Fairlawn NJ (USA)), as well as those designated "BTC" (Stepan Co. Northfield IL (USA)).

The quaternary ammonium compound of Constituent C) is desirably present in a minimum amount to provide the desired germicidal and sanitizing effects, as the blooming effect of the concentrate compositions when added to a larger volume of water have been found to be hindered by the inclusion of excessive amounts of the such quaternary ammonium compounds in the concentrate compositions. Generally, Constituent C is present in the concentrate compositions in amounts of up to 5 % by weight and less, preferably from 0.5 - 2 % by weight, and most preferably from 0.8 - 1.2 % by weight. It has also been found by the inventors that the preferred amounts are in part dictated by toxicological considerations as an excess of the cationic component may pose an increasing risk of irritation to the eyes, skin and mucocous tissues of a consumer.

Constituent E)

A further constituent of the concentrate compositions according to the invention are fragrances and/or fragrance enhancers which provide a characteristic pine oil scent and and scent longevity, particularly wherein the concentrate compositions are diluted to form cleaning compositions therefrom. As is described in the specification under claims, the term "fragrance" is used to refer to and to include any non-water soluble fragrance substance or mixture of such substances including those which are naturally derived (i.e., obtained by extraction of flower, herb, blossom or plant), those which are artificially derived or produced (i.e., mixture of natural oils and/or oil constituents), and those which are synthetically produced substances (odiferous substances).

Generally fragrances are complex mixtures or blends various organic compounds including, but not limited to, certain alcohols, aldehydes, ethers, aromatic compounds and varying amounts of essential oils such as from about 0 to about 85% by weight, usually from about 10 to about 70% by weight, the essential oils themselves being volatile odiferous compounds and also functioning to aid in the dissolution of the other components of the perfume. In the present invention, the precise composition of the perfume is of no particular consequence to cleaning performance so long as it may be effectively included as a constituent of the compositions. Generally however, one or more fragrances characteristic of pine oil type compositions, such as natural or synthetically produced fragrance compositions, especially those which are intended to mimic the scent of one or more resins or oils derived from coniferous species of trees, viz., a scent characteristic of pine oil type cleaning

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concentrates are used. Fragrance effects atypical of pine oil type cleaning concentrates may be used as well. Fragrance adjuvants for enhancing the scent effect of a fragrance, and/or for improving the miscibility of such fragrance compositions include known art fragrance adjuvants, for example, fenchol.

5 In any type of composition, the pine oil scent is the characteristic scent which is emitted by pine oil, and the longevity of such a pine oil scent is understood to be closely related to the pine oil content of a concentrate composition or a cleaning composition as described in this specification. Thus, it is normally expected that an increase in the pine oil provides an increase in the characteristic pine oil scent and in the scent longevity, however, for reasons noted earlier in this specification, the inclusion of increased amounts of pine oil is not always desirable from other standpoints. To provide a desired characteristic pine oil scent and pine oil scent longevity without requiring an increased amount of pine oil, the present inventors have found that by careful selection of fragrances and/or fragrance enhancers a reduction in the amount of pine oil may be achieved while maintaining a characteristic pine oil scent and a scent longevity. At the same time, this has been achieved without undesirably effect the blooming behavior of pine oil cleaning compositions taught herein. Also, a further undesired characteristic is an expectation of increased irritancy especially to the eyes, skin and mucocous tissues which an increase in an organic solvent such as a fragrance/fragrance solubilizer which is known to emit a volatile fraction has been avoided.

10 Constituent F) Water is added in order to provide 100% by weight of the concentrate composition. The water may be tap water, but is preferably distilled and/or deionized water. Water is added in amounts which are sufficient to form the concentrated compositions which amount is sufficient to ensure the retention of a substantially clear characteristic when produced as a concentrate, but at the same time ensuring good blooming upon the addition of the concentrated composition to a further amount of water, or upon the addition of further water to the concentrate. 25 Generally, water is present in the concentrate compositions in amounts in excess of about 80% by weight, preferably in amounts of in excess of 75% by weight, but most preferably in amount of between 60 -70 % by weight based on the total weight of Constituents A - F in the concentrate compositions taught herein.

30 Optional constituents: Further optional, but advantageously included constituents are one or more coloring agents which find use in modifying the appearance of the concentrate compositions especially to impart to concentrate compositions an appearance characteristic of a pine oil type concentrate composition. However, other colors atypical of pine oil type cleaning concentrates may be used as well. Known art light stabilizer constituents which act to retain the appearance characteristics of the concentrate

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compositions over longer intervals of time may also be used. Further optional constituents may also be used which, by way of non-limiting example include pH adjusters, pH buffering agents, foaming agents, further surfactants including anionic, cationic, non-ionic, amphoteric and zwitterionic surfactants, especially those useful in providing further deterative effects, and water softening agents.

5 These optional, i.e., non-essential constituents should be selected so to have little or no detrimental effect upon the desirable characteristics of the present invention, namely the blooming behaviour, cleaning efficacy, disinfectant activity, and low toxicity as provided by the inventive compositions, an in most cases anionic surfactants which may deactivate the quaternary cationic surfactant are to be avoided. Generally the total weight of such further conventional additives may comprise up to 10%

10 by weight of a concentrated composition formulation.

The term "concentrate" as used in this specification is the pre-consumer dilution and the composition of the cleaning composition which is the typically the form of the product prepared for sale to the consumer or other end user. The term "cleaning compositions" are the water diluted compositions which are expected to be prepared by the consumer or other end user by mixing a

15 measured amount of the "concentrate" with water in order to form an appropriately diluted cleaning composition which is suitable for use in cleaning applications, especially in the cleaning of hard surfaces. Such may be easily prepared by diluting measured amounts of the concentrate compositions in water by the consumer or other end user in certain weight ratios of concentrate:water, and optionally, agitating the same to ensure even distribution of the concentrate in the water. As noted,

20 the concentrate may be used without dilution, i.e., in concentrate:water concentrations of 1:0, to extremely dilute dilutions such as 1:10,000. Desirably, the concentrate is diluted in the range of 1:0.1 - 1:1000, preferably in the range of 1:1 - 1:500 but most preferably in the range of 1:10 - 1:100. It is to be understood however that the "concentrate" composition without any further dilution and it may be used "as is."

25 It is also to be understood, that the percentages of the constituents have been generally referred to in this specification as percent by weight or as parts by weight based on a measure of 100 % by weight, unless otherwise indicated.

Example Formulations:

Preparation of Example Formulations:

30 Exemplary formulations as illustrated on Table 1 following according to the instant invention were prepared in accordance with the following general procedure.

Into a suitably sized vessel, the following constituents were added in the following sequence: pine oil, co-solvent, nonionic surfactant system, fragrance/fragrance enhancer, cationic surfactants, water and lastly, optional constituents. The order of mixing is not critical in order to achieve

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concentrate compositions exhibiting the desired results. All of the constituents were supplied at as weight percentages, as room temperature, and mixing of the constituents was achieved by the use of a magnetic stirrer. Mixing, which generally lasted from 1 minute to 15 minutes, was maintained until the particular exemplary formulation attained uniform color and uniform clarity. Each of the

5 formulations exhibited the following physical characteristics: transparent appearance, light orange to medium orange-brown color, and a noticeable pine oil odor. The exemplary formulations were readily pourable, and retained well mixed characteristics (i.e., stable mixtures) upon standing at room temperature (about 68°F) for periods in excess of several weeks. The stability of the concentrate

10 formulations was also evaluated at by heating to 120°F determine if clouding or phase separation occurred; none was observed.

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Table 1: Formulations								
Constituent:	E1	E2	E3	E4	E5	E6	E7	E8
Pine Oil 1	8	--	--	--	--	8	8	8
Pine Oil 2	--	8	5	5	6	--	--	--
Isopropanol	9.25	9	5	5	4	9.25	9.25	9.25
diethylene glycol n-butyl ether	--	--	6	6	5	--	--	--
Poly-Tergent® SL-62	8	8	8	8	8.75	8	8	8
Neodol® 91-2.5	5	5	4	4	1.75	5	5	5
alkyldiethanolamide	1.4	1.2	1	--	1	1.18	1.5	1.8
BTC-8358	0.9	0.9	1	1	1	0.9	0.9	0.9
BTC-818	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Fragrance I	1.2	--	--	--	--	--	1.2	1.2
Fragrance II	--	0.1	0.1	0.1	0.1	--	--	--
Fragrance III	--	--	--	--	--	0.6	--	--
fenchol	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
coloring agent	0.001	0.0008	0.0008	0.0008	0.0008	0.0008	0.0008	0.0008
Deionized water	65.65	67.2	69.29	70.29	71.8	66.47	65.55	65.25

Pine Oil 1 is a pine oil preparation containing at least about 60% terpene alcohols

Pine Oil 2 is a pine oil preparation containing at least about 80% terpene alcohols

Poly-Tergent® SL-62 is a nonionic alkoxyethylated linear alcohol surfactant

Neodol® 91-2.5 is a nonionic surfactant composition based on linear alcohol ethoxylates featuring a cloud point < 20°C

BTC-8358 is an alkyl benzyl dimethyl ammonium chloride (80% active) available from Stepan Chemical Co.

BTC-818 is a dialkyl dimethyl ammonium chloride (50% active) available from Stepan Chemical Co.

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The determination of the amount of a solubilizing agent, here isopropyl alcohol, required in order to clarify the formulations of Table 1 provides a useful indication of the amount of required co-solvents which are required in typical concentrate formulations. The weight percent of isopropyl alcohol (100%) which was added to each of the formulations is also indicated on Table 1. It is to be noted that the values indicated on Table 1 are on a 100% total weight basis of the actual weight percentages of the constituents added.

Preparation of Cleaning Compositions:

Cleaning testing was performed utilizing one or more of the exemplary compositions within the scope of the invention as illustrated on Table 1, and cleaning compositions prepared from known commercially available cleaning products, which are indicated as comparative examples.

Comparative Example "C1":

A cleaning composition was formed by forming an aqueous dilution of one part by weight of Lysol® Pine-Action Cleaner, a commercially available cleaning concentrate with 64 parts by weight of water at approximately 20°C and subsequently manually stirring the same to form a uniform mixture.

Comparative Example "C2":

A cleaning composition was formed by forming an aqueous dilution of one part by weight of Spic and Span® Ultra Pine Deodorizing Cleaner, a commercially available cleaning concentrate with 128 parts by weight of water at room temperature (approx. 20°C) and subsequently manually stirring the same to form a uniform mixture.

Comparative Example "C3":

A cleaning composition was formed by mixing one part of a commercially available cleaning formulation, PineSol® Cleaner, a pine oil type cleaning concentrate, with 64 parts of water at room temperature, approximately 20°C, and manually stirring the same to form a cleaning composition therefrom.

Cleaning Evaluations:

Cleaning evaluations were also performed in accordance with the testing protocol outlined according to ASTM D4488 A2 Test Method, which evaluated the efficacy of the cleaning compositions on masonite wallboard samples painted with wall paint. The soil applied was a greasy soil sample containing vegetable oil, food shortening and animal fat. The sponge (water dampened) of a Gardner Abrasion Tester apparatus was squirted with a 15 gram sample of a tested cleaning composition, and the apparatus was cycled 10 times. The evaluation of cleaning compositions was "paired" with one side of each of the test samples treated with a composition according to the invention, and the other side of the same sample treated with a comparative example's composition,

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thus allowing a "side-by-side" comparison to be made. Each of these tests were duplicated on 20 wallboard tiles and the results statistically analyzed and the averaged results reported on Table 2, below. The cleaning efficacy of the tested compositions was evaluated utilizing a Minolta Chroma Meter CF-110, with Data Processor DP-100, which evaluated spectrophotomic characteristics of the sample. The results are reported on Table 2 following.

Table 2				
composition comparative composition	E1 C1	E1 C2	E1 C3	E2 C3
reflectance reading: composition comparative composition	69.04 67.19	63.68 62.22	70.93 69.82	65.63 65.14

With respect to the results reported on Table 2 a value of "100" is indicative of a white (unsoiled) background, and a "0" value is indicative of a black background. A soil laden (uncleaned) surface generally provided a result of about 20-30.

As can be seen from the results of Table 2, the cleaning efficacy of the composition according to the invention provided favorable results with those of known art cleaning products.

1. Evaluation of Light Transmittance ("Blooming") of Formulations:

Each of the formulations described on Table 1 was evaluated to determine the degree of light transmittance, a measure of the opacity of each of these concentrated formulations. Also evaluated were comparative formulations designated as "C1" and "C2" as described above.

These aqueous dilutions were prepared to evaluate the degree of light transmittance, a measure of the opacity as well as of the blooming of each of the aqueous dilutions. Certain of these aqueous dilutions were also evaluated to determine the antimicrobial efficacy of the aqueous dilution. The results of the light transmittance evaluation was determined as a percentage of light transmitted through a sample of a particular aqueous dilution wherein the transmission of a like sample of water is assigned a percentage of 100%. Testing was performed by mixing a 3 g aliquot of a particular example formulation with 192 g of tap water (with approx. 100 ppm hardness) which formed a 1:64 dilution of the example formulation:water, after which the sample was mixed for 60 second and a transmittance reading was taken using a Brinkman model PC801 dipping probe colorimeter, which was set at 620 nm to determine the light transmission of each of the samples. Samples of each formulation at 20°C and at 40°C were evaluated, as well as the reference (pure tap water) sample used to calibrate the colorimeter to the reference 100% light transmission sample outlined above. The resulting determined values, reported in Table 3 below provide an empirical evaluation, reported in percent transmittance ("%T") of the degree of transparency of a diluted example formulation wherein 0% indicates complete opacity and 100% the transparency of a water sample as noted above.

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Accordingly, a lower %T of a particular aqueous dilution provided a more desirable indication of the blooming characteristic of the particular aqueous dilution.

Table 3 - Percentage Light Transmittance (%T)								
Light Transmittance:	E1	E3	E4	E5	E7	E8	C2	C3
%T at 20°C	30-40	30-40	>80	>80	20-30	10-20	>80	>80
%T at 40°C	10-20	30-40	--	--	10-20	<10	>80	>80

- 5 As may be seen from the results described on Table 3, the formulations according to the invention were comparable to, but in most cases better than the known art formulations represented by the Comparative examples, C1 and C2.

2. Evaluation of Light Transmittance ("Blooming") of Formulations:

- 10 Further formulations according to the invention as well as further "comparative" formulations were produced; their constituents are noted on Table 4 below. The individual constituents were the same as used for the formulations of Table 1, but for the use of a different coloring agent (1% indicates weight actives) and a different fragrance.

Table 4				
	C4	C5	E9	E10
Constituents				
Pine Oil 80	8.00	8.00	8.00	8.00
Isopropanol	9.25	9.25	9.25	9.25
Polytergent® SL-62	8.00	8.00	8.00	8.00
Neodol® 91-2.5	5.00	5.00	5.00	5.00
alkyldiethanolamide	0.00	0.50	1.50	2.00
Fenchol	0.10	0.10	0.10	0.10
Fragrance	1.20	1.20	1.20	1.20
BTC-8358	0.90	0.90	0.90	0.90
BTC-818	0.50	0.50	0.50	0.50
coloring agent (1%)	0.11	0.11	0.11	0.11
Deionized Water	66.94	66.44	65.44	64.94

- 15 In a similar manner to that described above, the blooming characteristics of the further compositions according to the invention (designated as "E9" and "E10") as well as further comparative examples (designated as "C4", "C5") were evaluated as to their blooming characteristics by forming a 1:64 dilution of a respective example or comparative formulation in water, after which the sample was mixed for 60 seconds and a transmittance reading was taken using a Brinkman
- 20 model PC801 dipping probe colorimeter set at 620 nm to determine the light transmission of each of

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the samples. Samples of each formulation at 20°C and at 40°C were evaluated and the percentage light transmittance is reported on Table 5 below.

Table 5 - Percentage Light Transmittance (%T)				
	C4	C5	E9	E10
Bloom at 20°C	97	97	28	13
Bloom at 40°C	86	92	11	2

5 As may be seen from Table 5, the formulations according to C4 and C5 having low amounts of diethanolamide and high levels of fragrance (1.2%wt.) exhibited high percentages of light transmitted, indicating very poor blooming characteristics. In sharp contrast, the formulations according to E9 and E10 having the same level of fragrance, but including at least about an equivalent amount of (in %wt.) of the diethanolamide as the fragrance featured surprisingly and substantially improved blooming characteristics as demonstrated by low high percentages of light transmitted.

Evaluation of Scent Longevity:

An evaluation of the scent longevity of formulations of Example formulation "E1" described on Table 1 above, compared to a comparative formulation "C1" was performed.

15 Individual cleaning composition based on each of these formulations was produced by mixing 4 grams of a respective formulation with 256 grams of water, which formed a representative 1:64 dilution, typical of the dilutions used for such pine oil type products in domestic environments. Next, each of these cleaning compositions was poured onto a floor surface in separate rooms and mopped with a sponge mop to cover approximately 40 square feet of floor surface with a cleaning composition. Circulation fans were turned on for 5 minutes and then turned off. Within 1/2 hour of mopping, two groups each consisting of 20 test panelists were asked to enter one of the rooms, stay in the room for 45 seconds, and then exit the room. Subsequently, each panelist was asked to evaluate the scent emanated by the floor, and remain outside of both test rooms in order to allow for their nasal passages to clear and become accustomed to the ambient. Afterwards, the members of the group were asked to enter the other of the two rooms, again stay in the room for 45 seconds, exit the room, and evaluate the scent emanated by the floor in the room just visited.

25 After a time interval of 7 hours after mopping, and again after a 24 hour interval after mopping, each of the members of the groups repeated the above protocol, and again evaluated the scent emanated by the two treated flooring surfaces at these two later time periods. In such a manner, a meaningful evaluation of the relative pine scent, especially after the longer time periods of 7 and 24 hours after application could be obtained, and compared to a presently commercially available pine oil type cleaning composition.

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Table 6 - Scent Duration Characteristics			
Cleaning Composition: 1 part formulation: 64 parts water	Strength of pine scent: 1/2 hour after application	Strength of pine scent: 7 hours after application	Strength of pine scent: 24 hours after application
C1	44%	16%	33%
E1	56%	84%	67%

The numbers indicated on Table 6, as well as graphically illustrated on Figure 1, the total percentages of the group who indicated preference for one formulation's scent over that of the other. As can be seen, while the results following the first one-half hour following application are not dissimilar, the strength of the pine oil scent left by the formulations according to the invention as exemplified by E1 are significantly stronger, and exhibit a greater duration than that of the prior art formulation, C1.

Evaluation of Ocular Irritation:

The ocular irritation characteristics of formulations according to the invention were evaluated using the known Draize Eye test protocol. Evaluation was performed on a formulation according to Example E7 of Table 1 above in an "as is" composition, namely without any further dilution. As known, the Draize Eye Test measures eye irritation for the grading of severity of ocular lesions, with separate scores obtained for the cornea, iris and conjunctiva. For the cornea, after exposure to the composition, A the cornea opacity is graded on a scale from 1-4; B the area of cornea involved is graded on a scale from 1-4 (where the score = A x B x 5 may be a total maximum of 80). For evaluation of the iris, after exposure the composition, A the involvement of the iris is graded on a scale of 1-2 (where the score = A x 5 may be a total maximum of 10). For a evaluation of the conjunctive, A Redness is graded on a scale of 1-3; B Chemosis is graded on a scale of 1-4; and C Discharge is measured on a scale of 1-3 [where the score = (A + B + C) x 2 may be a maximum of 20]. The maximum total score is the sum of all scores obtained for the cornea, iris and conjunctive (a maximum of 110).

The Draize test score on day 1 of the test was 19.33, and it was further observed that all signs of opacity cleared in all of the 6 subjects by day 7 of the test, although conjunctival irritation was observed in 1 of the 6 test subjects by day 7. The Draize score on day 7 of the test was 0.33. By day 14, all signs of any irritation, opacity or conjunctival irritation was observed to have cleared. The results of the Draize test indicated than an EPA Tox Category "0" was appropriate. That these results were achieved with a product known to have a significant content of constituents which individually considered are known irritants was particularly surprising.

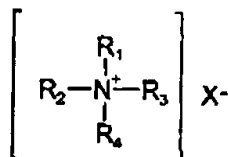
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Claims:

1. A blooming type, pine oil type cleaning concentrate composition comprising the following constituents:
 - 5 A) a pine oil preparation containing at least about 60% alpha-terpineol;
 - B) a co-solvent;
 - C) a non-ionic surfactant system which includes two or more non-ionic surfactants wherein at least one of which exhibits a cloud point of 20°C or less in water;
 - D) a cationic quaternary ammonium surfactant which exhibits germicidal activity;
 - 10 E) a fragrance/fragrance enhancer; and,
 - F) water.
2. The pine oil type cleaning concentrate according to claim 1 wherein:
 - 15 B) is selected from: C₁-C₈ alcohols, glycol ethers and glycols.
3. The pine oil type cleaning concentrate according to claim 1 wherein:
 - C) includes a alkoxyated linear alcohol surfactant.
4. The pine oil type cleaning concentrate according to claim 1 wherein:
 - 20 C) includes a monoalkanolamide, dialkanolamide or trialkanolamide surfactant composition.
5. The pine oil type cleaning concentrate according to claim 1 wherein:
 - D) is a quaternary ammonium compound which exhibits germicidal activity according to the structure:



25 wherein;

at least one of R₁, R₂, R₃ and R₄ is selected from hydrophobic, aliphatic, aryl aliphatic or aliphatic aryl radical of from 6 to 26 carbon atoms, and any remaining R₁, R₂, R₃ and R₄ are hydrocarbons of from 1 to 12 carbon atoms, wherein any of R₁, R₂, R₃ and R₄ may be linear or branched and may include one or more ether or amide linkages; and,

30 X is a salt-forming anionic radical.

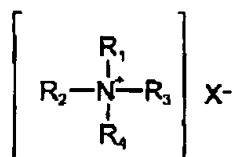
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6. A pine oil type cleaning concentrate comprising the following essential constituents:

- A) 0.001 - 15% by weight of a pine oil preparation comprising at least 60% alpha-terpineol;
- 5 B) 0.001 - 15% by weight of a co-solvent selected from selected from: C₁-C₈ alcohols, glycol ethers and glycols;
- C) 0.001 - 15 % by weight of a nonionic surfactant system which comprises two or more nonionic surfactants wherein at least one of said nonionic surfactants exhibits a cloud point of 20°C or less in water;
- 10 D) 0.5 - 5% by weight of a cationic quarternary ammonium compound according to the structure:



wherein;

- 15 at least one of R₁, R₂, R₃ and R₄ is selected from hydrophobic, aliphatic, aryl aliphatic or aliphatic aryl radical of from 6 to 26 carbon atoms, and any remaining R₁, R₂, R₃ and R₄ are hydrocarbons of from 1 to 12 carbon atoms, wherein any of R₁, R₂, R₃ and R₄ may be linear or branched and may include one or more ether or amide linkages; and,
- X is a halide or methosulfate radical;
- 20 E) 0.000001 - 1.5% by weight of a fragrance/fragrance enhancer; and,
- F) to 100% by weight, water.

7. A blooming type, pine oil type cleaning composition according to claim 1 or 6 which further comprises up to 10% by weight based on the total weight of the cleaning composition of one or more nonessential constituents selected from: coloring agents, light stabilizers, pH adjusters, pH buffering agents, foaming agents, further surfactants including anionic, cationic, non-ionic, amphoteric and zwitterionic surfactants, and water softening agents.

25

8. A blooming type, pine oil cleaning composition according to claim 1 or 6 wherein constituent C) is present in a weight percentage about equal to, or greater than the amount of constituent E) present in the said composition.

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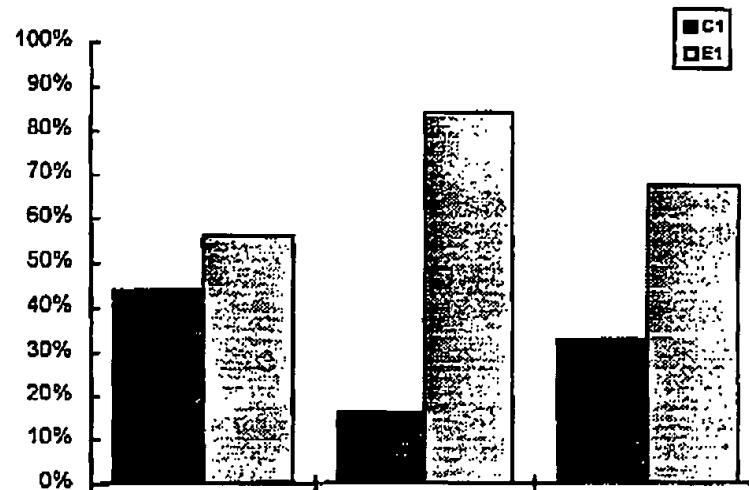
9. An aqueous cleaning composition comprising the pine oil type cleaning concentrate composition according to claim 1 or 6 dispersed in water in a weight ratio of concentrate composition:water of from 1:0.1 to 1:1000.
- 5
10. A process for process for cleaning and disinfecting a hard surface requiring such treatment which process includes the step of:
- applying the composition according to claim 1 in an amount effective for providing cleaning and/or disinfecting treatment.
- 10

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I/I

Figure 1



INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/15588

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C11D 1/68, 1/72, 1/835, 3/43, 3/44, 3/50
US CL : 510/214, 421, 422, 423, 433, 416, 463, 504

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 510/214, 421, 422, 423, 433, 416, 463, 504

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS,
search terms: pine oil, terpene alcohol, terpineol, cationic, quaternary, germicide, nonionic

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, 3,666,668 A (KLAUSNER) 30 May 1972, see abstract, col. 2 lines 46-59, col. 3 lines 8-13, col. 5 lines 39-43, col. 4 lines 33-50 and example 4.	1-3, 7-10
Y	CA, 1,120,820 A (REBARBER et al.) 30 March 1982, see page 1 lines 17-29, page 2 lines 1-10, page 3 lines 1-6 and example 2.	1-3, 5-10
Y	US, 5,435,935 A (KUPNESKI) 25 July 1995, see abstract, col. 4 lines 27-82, col. 5 line 62 to col. 6 line 17, col. 8 lines 25-32 and claim 1.	1-10
Y	US 4,597,887 A (COLODNEY et al.) 01 July 1986, see abstract, col. 4 lines 20-35, col. 3 lines 8-16 and example 1.	1-10

☒ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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"L" document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another claim or other special reason (to be specified)

"O" documents referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principles or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"Z" document member of the same patent family

Date of the actual completion of the international search

16 JANUARY 1997

Date of mailing of the international search report

11 MAR 1997

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Form PCT/ISA/210 (second sheet) (July 1992)*

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/15588

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category ^a	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
T	US, 5,591,708 A (RICHTER) 07 January 1997, see abstract	1-10

Form PCT/ISA/210 (continuation of second sheet) (July 1992)*